

Simultaneous HDS and HDN over supported PtSn catalysts in comparison to commercial NiMo/Al₂O₃

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Received 11 July 2007; received in revised form 28 September 2007; accepted 4 October 2007

Available online 13 October 2007

Abstract

The performance of platinum-tin catalysts, supported on Al₂O₃ and SiO₂ and subjected to reduction prior to use, has been studied. The catalysts were characterized in reduced forms by X-ray diffraction (XRD) and XPS. The surface properties were determined by N₂ BET specific surface area and CO chemisorption. The model compounds were 4,6-dimethylbenzothiophene (4,6DMDBT) and carbazole. The PtSn catalysts supported on either Al₂O₃ or SiO₂ were characterised by high activity, but the catalyst PtSn/SiO₂ was found the most effective, even more effective than the commercial KF848 catalyst. Both PtSn catalysts studied were more effective in the reaction of 4,6DMDBT hydrogenation, the dominant product obtained with the use of PtSn/Al₂O₃ was methyl-cyclohexyltoluene (MCHT) and with PtSn/SiO₂ the dominant product was dimethylbicyclohexyl (DMBCH). The amount of dimethylbiphenyl (DMBPh) obtained was small and practically independent of the contact time. In the HDN reaction of carbazole the most active was PtSn/SiO₂. It was also more active in the consecutive reaction of isomerisation of the main product of the HDN reaction, bicyclohexyl (BCH) to methylcyclopentylcyclohexane (MCPCH). The large differences shown in the hydrotreating activity specially in the HDN reaction between PtSn catalysts supported on Al₂O₃ and SiO₂ result from the physicochemical properties of both samples. The significantly higher CO chemisorption for PtSn/SiO₂ indicates the presence of larger amount of metallic species and better hydrogenation properties so important for deep hydrotreating process.

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Keywords: Hydrodesulphurisation; Hydrodenitrogenation; 4,6-Dimethylbenzothiophene; Carbazole; Platinum; Tin; Alumina and silica supports; Commercial catalyst-KF848

1. Introduction

The necessity of introducing more drastic measures for the environment protection implies among others the need for searching for new effective methods of sufficiently deep hydrotreating of engine fuel to satisfy the demands as to the content of heterocompounds in commercially available fuel. It has been planned that in this year the content of sulphur in diesel oil should not exceed 50 ppm (0.005%), and in 2006—even 15 ppm (0.0015%) in the USA, while 10–50 ppm (0.001–0.005%) in EU. In 2009, the fuels containing less than 10 ppm sulphur are scheduled to be introduced [1]. To be able to meet these requirements, the application of technological solutions based on two-stage hydrotreating is planned. On the other hand,

the search for more active catalysts is continued. Usually, new catalysts have been obtained by a modification of the support with, e.g. fluoride or boron ions [2,3] or by use of different supports or their mixtures [4–6]. The idea of using systems containing noble metals as promoters, e.g. platinum, is relatively new. After the first stage of hydrotreating, the product contains on average 250–300 ppm sulphur and about 100 ppm nitrogen [7] and the removal of these substances is much more difficult because they are resistant to desulphurization and denitrogenation. In view of the above, new catalysts of the second stage of hydrotreating should have other properties than those used hitherto, e.g. should have higher hydrogenation activity [8].

It is known that the two-stage hydrotreating process using noble metal catalysts in the second stage can ensure deep levels of aromatic hydrogenation under mild operating conditions, such as moderate hydrogen pressure and lower temperature. It has been established that noble metal catalysts are easily poisoned by small amounts of sulphur. Therefore, in recent

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years, extensive studies have been performed to develop sulphur-tolerant noble metal catalysts for the two-stage hydrotreating process [9–12].

Hitherto literature gives relatively little information on the application of bimetallic systems containing noble metals in hydrodesulphurisation (HDS) [13–16] and hydrodenitrogenation (HDN) reactions. The catalyst containing only one metal, e.g. platinum, is not resistant to deactivation because of the coke formation [17]. The presence of another metal improves the catalyst activity in HDS and hydrogenation reaction [15], and the sulphur present on the catalyst surface is labile and takes part in the HDS reaction [16].

Barias et al. [18] reported that the effect of Sn as a promoter depends on the support. On γ -Al₂O₃, tin interacts with the support and after reduction it is stabilized in an oxidation state >0. Moreover, platinum supported on the tin containing medium is more dispersed and such a catalyst is characterised by improved stability and higher activity in the reaction of dehydrogenation. On SiO₂, Sn is more readily reduced, and alloy formation with platinum is possible. Moreover, the presence of tin increases Pt dispersion and improves the stability of thus obtained catalyst.

Paal et al. [19] studied the effect of hydrogen pressure in the reaction of *n*-hexane. The PtSn/Al₂O₃ from the bimetallic precursor contains the two metals in a better dispersion, resulting in a larger number of atomically dispersed surface Pt active sites. The catalyst studied has good thermal stability and gives more isomers in comparison with the monometallic Pt/Al₂O₃ catalyst. On the other hand, it has a lower aromatic selectivity.

Passos et al. [20] observed that the presence of Sn improves the stability and activity of the platinum catalysts in the *n*-heptane conversion. Bednarova et al. [21] also reported that the presence of the second metal (Sn) enhances the stability of the platinum catalyst through reduction of coking.

In general, the promotion of monometallic Pt catalysts by Sn has several advantages: it prevents the hydrogenolytic effect of platinum, favours the selectivity of the dehydrogenation reactions, mitigates the sintering effect, and decreases the deactivation rate caused by carbon formation [21].

Hydrotreating is still one of the most important processes in refineries [22,23]. Increasing demands have promoted a study of deep hydrodesulphurisation [24–26], therefore, the model compounds for catalysts testing have been chosen 4,6-dimethyldibenzothiophene and carbazole, known to be difficult subjects of hydrodesulphurisation and hydrodenitrogenation.

Till now the PtSn catalytic system were not applied in hydrotreating reactions. The literature data mentioned above indicate positive influence of tin on PtSn catalysts. So we have decided to applied these catalysts for the hydrotreating process.

2. Experimental

2.1. Catalysts

For the preparation of catalysts were used two supports: Al₂O₃ (Norit) and SiO₂ (Cab-O-Sil). The catalysts were

obtained by the using the relevant solutions of platinum that was deposited using a solution of hexachloroplatinic acid—H₂PtCl₆, while tin was deposited from tin (IV) chloride—SnCl₄. Each support was impregnated in one step by incipient wetness (pore filling) method by coimpregnation applying an appropriate amount of H₂PtCl₆ and SnCl₄. After the impregnation the samples were dried at room temperature for 2 h, at 80 °C for 2 h and finally overnight at 120 °C. Nominal concentration of Pt and Sn were equals 3 wt%.

2.2. CO chemisorption

The CO uptake was performed “*in situ*” after reduction (H₂, 400 °C) in quartz reactor without exposing the fresh catalysts to air. Pulses of a known quantity of CO (17 μ mol) were injected, at regular intervals, on the sample at RT in flowing He (40 $\text{cm}^3 \text{ min}^{-1}$) purified by an oxygen trap (Oxysorb, Messer Griesheim). After each injection, the quantity of probe molecules not chemisorbed was measured using a conventional device equipped with a TCD. The injections were continued until CO saturated the surface. Data were processed and the number of micromoles of CO chemisorbed per gram of sample could be determined.

2.3. Specific surface area

Specific surface area was measured for the samples after reduction *ex situ*. The reduction was performed in the same conditions as in the reactor before catalytic test. The specific surface area (S) of the samples was determined from the N₂ adsorption isotherms at 77 K on a ASAP2010 apparatus (Micromeritics).

2.4. XRD diffraction

Structural characterization of catalysts and supports, were carried out by X-ray diffraction using SIMENCE D-500 automatic diffractometer with the Cu K α monochromatized radiation.

2.5. XPS measurement

XPS measurements were performed using a SPECS PHOIBOS 100 hemispherical analyser equipped with a magnesium source (1253.6 eV) operating at 100 W (wide-range scan) and 200 W (high resolution spectra). The spectrometer energy scale was calibrated using Au 4f_{7/2}, Ag 3d_{5/2} and Cu 2p_{3/2} lines at 84.2, 367.9 and 932.4 eV, respectively. The analyser mode was set at constant pass energy of 30 eV in survey, and 5 eV in narrow scans. The detection angle was normal to the sample surface. The base pressure in the Ultra High Vacuum (UHV) analysis chamber was lower than 5×10^{-10} mbar. Energy shift due to the static charging of the samples was corrected with the C 1s peak at 284.6 eV as a reference. The spectra were collected and processed using SpecsLab software. The accuracy of the reported binding energies was ± 0.1 eV. Element concentra-

tions were evaluated from peak areas after Shirley background subtraction.

2.6. Catalytic test

Simultaneous reactions HDS and HDN were conducted with a down-flow fixed-bed microreactor in a high-pressure flow system. The catalyst (weight = 0.25 g, grain size 0.25–0.315 mm) was mixed with carborundum at a ratio of the catalyst to SiC = 1/5. The liquid feed was introduced to the reactor by means of a high-pressure piston pump. The hydrogen flow (30–360 cm³ min⁻¹) and total pressure were controlled by a mass flow controller and a back-pressure regulator, respectively. The temperature of the oven was regulated using a temperature controller.

The contact time (t_c) was defined as follows: t_c (s) = catalyst volume (cm³)/(H₂ flow + feed flow) (cm³ s⁻¹).

The total conversion (conv.) of 4,6DMDBT (carbazole) and degree of HDS or HDN was defined following:

$$\text{conv. of 4,6DMDBT [\%]} = \frac{S_S}{S_S + S_{4,6\text{DMDBT}}} \cdot 100\%;$$

$$\text{degree of HDS [\%]} = \frac{S_H}{S_S + S_{4,6\text{DMDBT}}} \cdot 100\%$$

where S_S is the molar % of all products of decomposition of 4,6-DMDBT (included S-derivatives), $S_{4,6\text{DMDBT}}$ is the molar % of 4,6-DMDBT in liquid product after reaction. S_H is molar % non-sulfur products of decomposition of 4,6DMDBT.

$$\text{conv. of carbazole [\%]} = \frac{N_N}{N_N + N_{\text{carbazole}}} \cdot 100\%;$$

$$\text{degree of HDN [\%]} = \frac{N_H}{N_N + N_{\text{carbazole}}} \cdot 100\%$$

where N_N is the molar % of all products of decomposition of carbazole (included N-derivatives), $N_{\text{carbazole}}$ is the molar % of carbazole in liquid product after reaction. N_H is the molar % non-nitrogen products of decomposition of carbazole.

The liquid products of the reaction were collected every hour in the condenser whose temperature was maintained at 288 K. Finally, this liquid was analysed (dodecane was used as a internal standard) by gas chromatography (HP 4890) using a capillary column (HP1, 30 m × 0.25 mm × 0.25 μm) and a FID detector. The product identification was confirmed by GC/MS analysis with capillary column (DB5, 30 m × 0.25 mm × 0.25 μm).

The HDS reaction of 4,6-dimethylbenzothiophene and HDN reaction of carbazole were performed simultaneously at 350 °C, H₂ pressure of 6.0 MPa, the H₂/feed ratio of 600. The liquid feed contained 0.17% 4,6DMDBT (300 ppm S) + 0.08% carbazole (100 ppm N) in decaline. The reactions were conducted for contact times between 0.06 and 0.40 s. Before the reactions the PtSn/SiO₂ and PtSn/Al₂O₃ catalysts were reduced *in situ* at 723 K (450 °C) for 2 h in hydrogen atmosphere.

The reference catalyst was NiMo/Al₂O₃-KF848, made by AKZO-NOBEL ALBEMARLE. Catalysts which was used for long time industrial hydrotreating. The catalyst contained 1–5% NiO, >20% MoO₃ and 5–10% P₄O₁₀.

The procedure for the KF848 catalyst activation given by the AKZO-NOBEL producer was applied—sulphidation in 2.5% DMDS solution in cyclohexane.

For each contact time the reactions were continued till getting a stable catalytic activity. The catalytic process was conducted for about 100 h. After this time the initial conditions of the reaction were reset (initial contact time) and the reaction was continued to obtained stable catalytic activity again (after about additional 15 h).

3. Results

3.1. Characterization of catalysts

3.1.1. CO chemisorption

The experimental CO uptakes of the sample of both catalysts (after reduction *in situ*) were 45.6 and 26.2 μmol g⁻¹ for PtSn/SiO₂ and PtSn/Al₂O₃, respectively. Amount of metallic phase is about two times higher for PtSn/SiO₂ than PtSn/Al₂O₃.

3.1.2. Specific surface area

The specific surface area of the both catalysts were 209 and 236 m²/g for PtSn/Al₂O₃ and PtSn/SiO₂, respectively. We can say, that specific surface area of both catalysts are similarly.

3.1.3. XRD diffraction

Fig. 1 shows the diffraction patterns of PtSn/SiO₂ catalyst compared to the pure SiO₂. For catalyst besides the four peaks additionally to the large pick from support (2θ = 22°) are presents. The first one for 2θ = 39.7° corresponds to alloys of Pt and Sn (PtSn₂), and other small two peaks for 2θ = 67.5° and 81.2° correspond to metallic platinum on the surface of SiO₂ [27]. The middle peak 2θ = 46.5° can be related to presence of metallic platinum or tin.

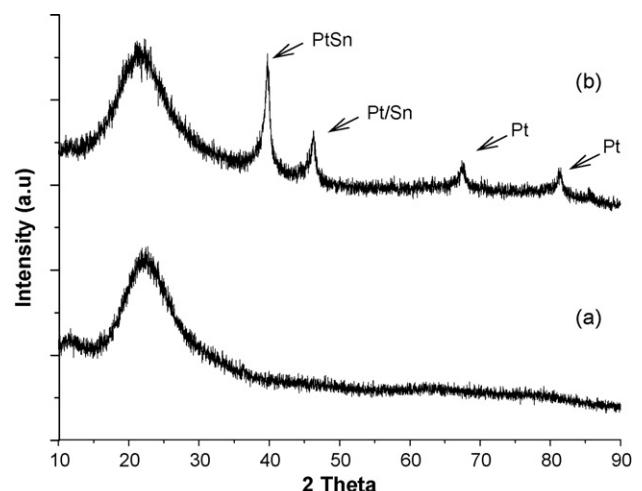


Fig. 1. XRD patterns for (a) SiO₂ and (b) PtSn/SiO₂.

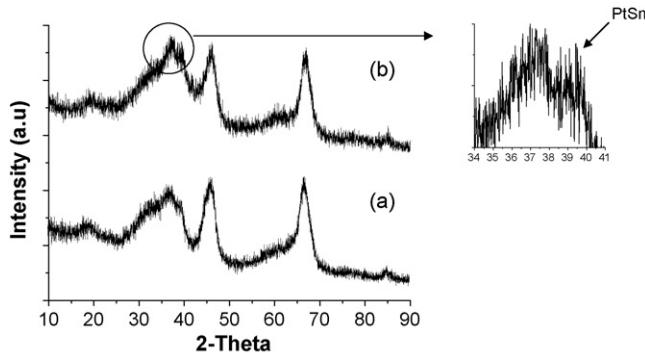


Fig. 2. XRD patterns for (a) Al_2O_3 and (b) PtSn/ Al_2O_3 .

XRD detected Al_2O_3 as the only crystalline phase in the PtSn/ Al_2O_3 sample (Fig. 2). In spite of this on the diffraction pattern of PtSn/ Al_2O_3 compare to pure Al_2O_3 we can observe small peak for $2\theta = 39.5^\circ$ which corresponded PtSn₂ alloys [27]. No peaks were found to correspond to the tin. It can suggest, that large amount of tin is present as subsurface as tin aluminate spinel [18].

3.1.4. XPS measurement

Fig. 3a and b displays the energy spectra of Sn3d_{5/2} tin, for PtSn/ Al_2O_3 and PtSn/ SiO_2 , respectively.

The tin spectrum (Fig. 3a; PtSn/ Al_2O_3) shows one maximum at 486.77 eV, which is higher than the energy for Sn^0 tin (483.3 eV). Thus, it points to a presence of oxidized Sn²⁺ tin and/or Sn⁴⁺ (FWHM—2.62 eV) [28,29]. Unfortunately, XPS cannot discriminate between Sn²⁺ and Sn⁴⁺ [30]. The result indicates that significant lower amount of metallic phase is formed on the PtSn/ Al_2O_3 surface under the catalyst's reduction; this has been also shown by measurements of CO chemisorption.

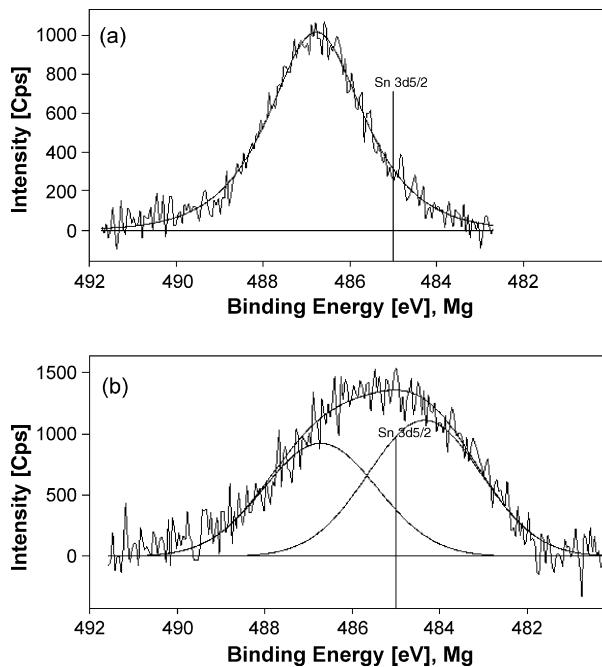


Fig. 3. XPS Sn3d_{5/2} spectra of the reduced catalysts. (a) PtSn/ Al_2O_3 ; (b) PtSn/ SiO_2 .

On the other hand, the Sn3d_{5/2} spectrum of PtSn/ SiO_2 (Fig. 3b) looks differently. The spectrum is characterized by a large half-width FWHM—3.06 eV. It implies the occurrence of Sn that is not in a single form. Deconvolution of the spectrum resulted in two peaks. One of them can be ascribed to Sn^0 , most likely occurring in an alloy with Pt. The other one seems to be due to oxidized Sn²⁺ form [28]. The intensities of the two peaks suggest that both forms are occurring in similar quantities. Sn^0 tin is likely to occur in PtSn alloys. The conclusion has been derived from XRD measurements which showed peaks ascribed to PtSn₂ alloy. However, even in that case, XPS cannot differentiate metallic Sn^0 from PtSn alloy [30].

Fig. 4a displays energy spectrum Pt4f_{5/2} of the catalyst PtSn/ SiO_2 . After the deconvolution, the spectrum shows four peaks. The two higher peaks, characterized by maxima at 71.09 and 74.39 eV, correspond to Pt⁰ platinum and/or PtSn alloys. As was already told, XPS cannot differentiate between the two forms [30,31].

The two lower maxima, 72.94 eV and 76.24 eV refer to Pt²⁺ platinum. However, an amount of the oxidized platinum is significantly lower compared with Pt⁰ (or PtSn alloys) [31].

For the PtSn/ Al_2O_3 catalyst, Fig. 4b displays exclusively a side spectrum of Pt4d_{5/2}. The reason why, is the occurrence of very intensive Al2p peak compared to the intensity of Pt4f peak. Besides the prevailing Pt⁰ form (313.8 eV), there is also the oxidized Pt²⁺ form with the energy shifted towards left >2 eV [29,32,33].

3.2. Hydrodesulphurisation

Fig. 5 presents the catalytic activity of the catalysts: PtSn/ Al_2O_3 and PtSn/ SiO_2 in the reaction of 4,6DMDBT conversion and in 4,6DMDBT hydrogenolysis (degree of HDS) versus the

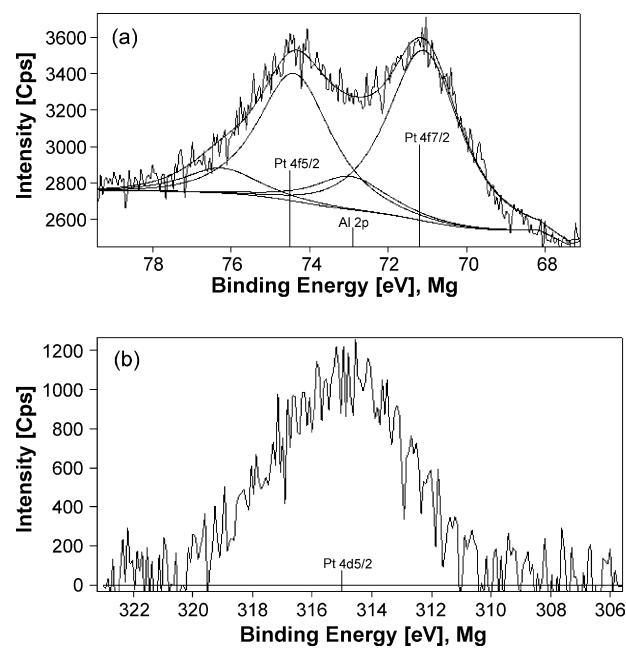


Fig. 4. XPS Pt4f_{5/2} spectra of the reduced PtSn/ SiO_2 catalyst (a); Pt4d_{5/2} spectra of the reduced PtSn/ Al_2O_3 catalyst (b).

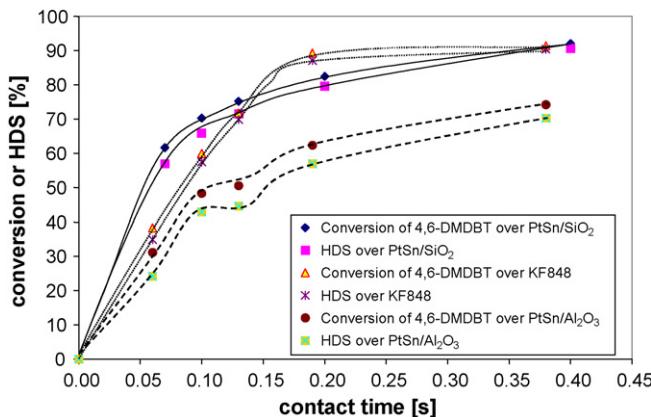


Fig. 5. Conversion and degree of HDS versus contact time for PtSn/Al₂O₃, commercial KF848 and PtSn/SiO₂ catalysts.

contact time. The results are compared with the data obtained for the commercial catalyst NiMo/Al₂O₃-KF848. The reaction of desulphurisation runs along two paths: through direct desulphurisation (DDS) to 3,3'-dimethylbiphenyl (3,3'DMBPh) and by destructive hydrogenation (hydrogenolysis) towards formation of methylcyclohexyltoluene (MCHT) and 3,3'-dimethylbicyclohexyl (3,3'DMBCH), with an intermediate of 4,6-dimethyl-tetrahydronaphthalene (4,6DMTHDBT), which is schematically shown in Scheme 1. The most active in the process of desulphurisation was PtSn/SiO₂. For the all range of contact time the catalyst PtSn/Al₂O₃ was less active than the commercial one. For this catalyst the difference between the total conversion and the degree of HDS in the whole range of the contact times studied was considerable, while for the commercial catalyst this difference was very small. Similarly small differences between the degree of HDS and total conversion were also observed in the presence of the catalyst PtSn/SiO₂. For the commercial catalyst KF848

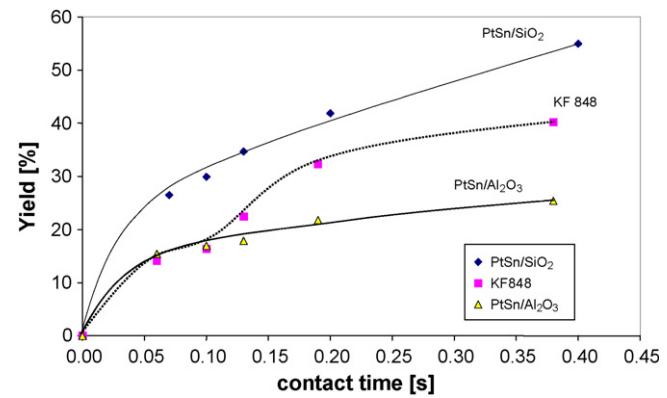


Fig. 6. Yield of methylcyclohexyltoluene (MCHT) as a function of contact time for PtSn/Al₂O₃, commercial KF848 and PtSn/SiO₂ catalysts.

the degree of desulphurisation and total conversion increases in linearly with increasing contact time (in range 0.06–0.13 s). An abrupt increase in both these degrees was observed for this catalyst for the contact times greater than 0.19 s, while the activity of PtSn catalysts increases in a monotonic way with the contact time. For the longest contact time the activities of PtSn/SiO₂ and the commercial KF848 catalyst were similar.

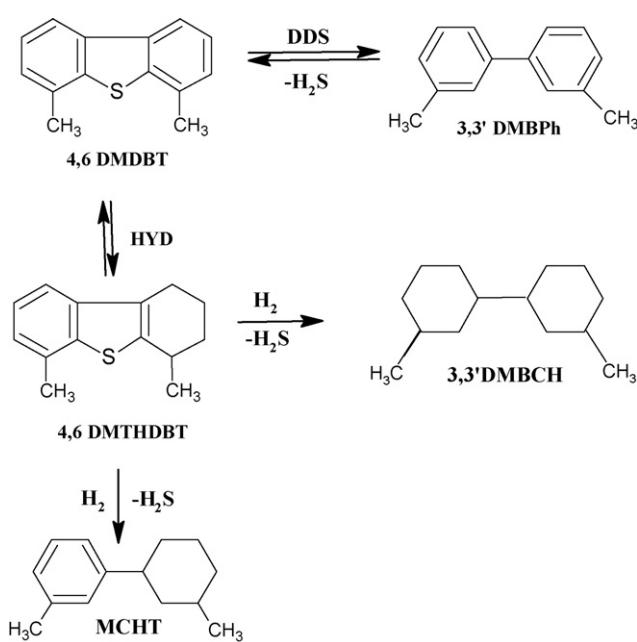
3.2.1. Distribution of MCHT

Fig. 6 presents a yield of MCHT being a product of hydrodesulphurisation of 4,6DMDBT followed by hydrogenation of 4,6DMTHDBT, versus the contact time. The yield of MCHT is defined as ratio of molar % of MCHT to sum of all molar % of all products of 4,6DMDBT conversion. High yield of MCHT was obtained with the use of PtSn/SiO₂ catalyst, whereas with the use of KF848 and PtSn/Al₂O₃ in the contact times 0.06–0.10 s the yield of MCHT was very similar. For the catalyst PtSn/Al₂O₃ the amount of MCHT obtained in the contact times 0.25–0.40 s was constant and at a level of about 20%. The yield of MCHT significantly increased for the commercial catalyst and for the contact times longer than 0.10 s. It should be emphasised that for the contact times applied, the increase in the MCHT yield for PtSn/Al₂O₃ was incommensurable relative to the increase in the contact times, while for the catalyst PtSn/SiO₂ the yield of MCHT increased in proportion to the increase in the time of contact.

The increase in the MCHT yield in proportion to the increase in the contact time observed for PtSn/SiO₂ indicates that for this catalyst the process of desulphurisation involves mainly hydrogenation (HYD) and not direct desulphurisation (DDS). Therefore, an increase in the conversion of 4,6DMDBT is related only to the increase in the yield of MCHT, which indicates that desulphurisation occurs by way of hydrogenation (HYD). A similar behaviour can be observed for PtSn/Al₂O₃, however, its activity towards MCHT formation is lower than that of PtSn/SiO₂.

3.2.2. Distribution of 3,3'DMBPh

Fig. 7 shows the yields of DMBPh in the presence of the catalysts studied. The highest yield of about 35% was obtained in the presence of the commercial KF848 catalyst in the whole



Scheme 1. Reaction network of the HDS of 4,6DMDBT.

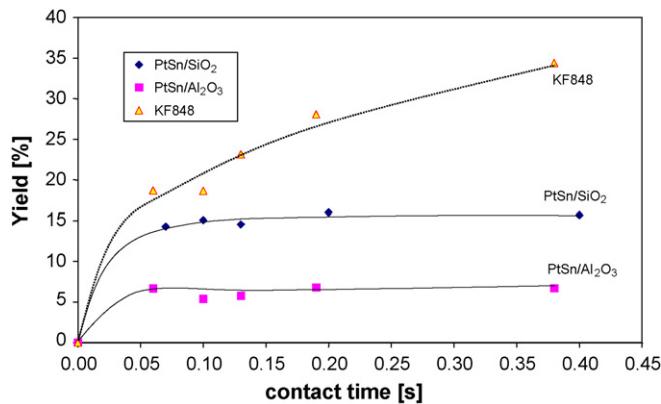


Fig. 7. Yield of dimethylbiphenyl (3,3'DMBPh) versus contact time for PtSn/Al₂O₃, commercial KF848 and PtSn/SiO₂ catalysts.

range of the contact times. In the presence of the PtSn catalysts the yields of DMBPh were practically at a constant level of 5 and 15% for PtSn/Al₂O₃ and PtSn/SiO₂, respectively. Thus, for both PtSn catalysts the yield of DMBPh was independent of the contact time.

3.2.3. Distribution of other products

The distribution of the other products of HDS of 4,6DMDBT desulphurisation in the presence of the PtSn catalysts is given in Figs. 8 and 9. As mentioned above, the reaction of desulphurisation in the presence of both PtSn catalysts occurs mainly through hydrogenation to MCHT and further to 3,3'DMBCH, while the process of DDS occurs to a lower degree. The time changes in the 4,6DMDBT concentration can be approximated by an exponential curve and the HDS process of 4,6DMDBT is an example of the subsequent reactions in which the intermediate product is 4,6DMTHDBT reaching a maximum concentration for the contact time of 0.07 s. In the presence of PtSn/Al₂O₃ (Fig. 6) and for the same contact time of 0.07 s the main reaction products were MCHT and 3,3'DMBPh. The amount of 3,3'DMBCH as the product of complete hydrogenation was very small. As mentioned earlier, for the contact time increasing above 0.07 s, the amount of MCHT (Fig. 6) insignificantly increases while the amount of 3,3'DMBCH

increases rapidly from about a few percent for the contact time of 0.07 s to about 20% for the time of contact of 0.10 s, and then increases in proportion to the contact time. For the catalyst PtSn/Al₂O₃ the main product of desulphurisation is 3,3'DMBCH. With the increasing contact time, the yields of both 3,3'DMBCH (Fig. 8) and MCHT increase (Fig. 6).

Assuming that 3,3'DMBCH is formed as a product of secondary hydrogenation of MCHT, the amount of the latter in any contact time would go through a maximum. As follows from Figs. 6 and 8, the amount of MCHT insignificantly increases with increasing contact time. Hence, it can be supposed that 3,3'DMBCH is formed as a product of direct hydrogenation of 4,6DMTHDBT. Therefore, there can be two parallel pathways of 4,6DMDBT hydrogenation: one leading to MCHT and the other giving direct hydrogenation of 4,6DMTHDBT to 3,3'DMBCH.

The distribution of the concentrations of the desulphurisation products obtained in the presence of PtSn/SiO₂ differs from that obtained in the presence of PtSn/Al₂O₃ (see Fig. 9). The former catalyst is much more active, which is evidenced by formation of the less hydrogenated product MCHT. Thus, it can be supposed that the HDS reaction over this catalyst occurs mainly through hydrogenation of the aromatic ring. In the presence of PtSn/SiO₂ the reaction of hydrogenation leading to the formation of MCHT (whose amount increases with increasing contact time) is more favoured than in the presence of PtSn/Al₂O₃. Again, in the presence of PtSn/SiO₂ the direct hydrogenation of 4,6DMTHDBT to 3,3'DMBCH occurs to a lower degree and the amount of 3,3'DMBCH formed does not depend on the contact time. It has been shown that the yields of 3,3'DMBCH (Fig. 9) and 3,3'DMBPh (Fig. 7) for the contact time longer than 0.1 s are practically constant.

The distribution of the other products of HDS of 4,6DMDBT in the presence of the commercial KF848 catalyst is presented in Fig. 10. The maximum amount of 3,3'DMBCH as the product of complete hydrogenation for the contact time 0.19 s was equal to 28%. For this contact time the amount of 3,3'DMBPh was similar (Fig. 7). The intermediate product is 4,6DMTHDBT reaching a maximum concentration for the contact time of 0.06 s.

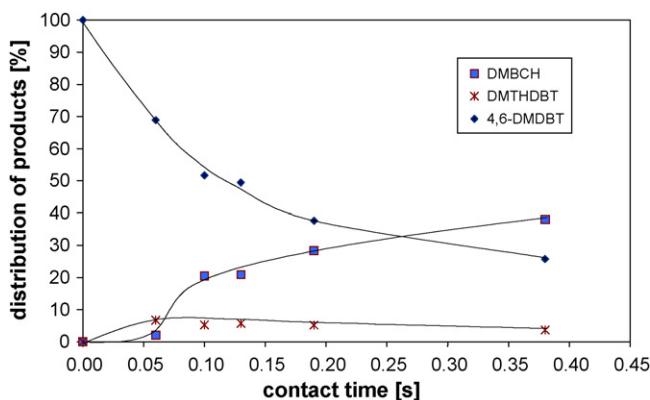


Fig. 8. Distribution of products for HDS of 4,6DMDBT change with the contact time over PtSn/Al₂O₃ catalyst.

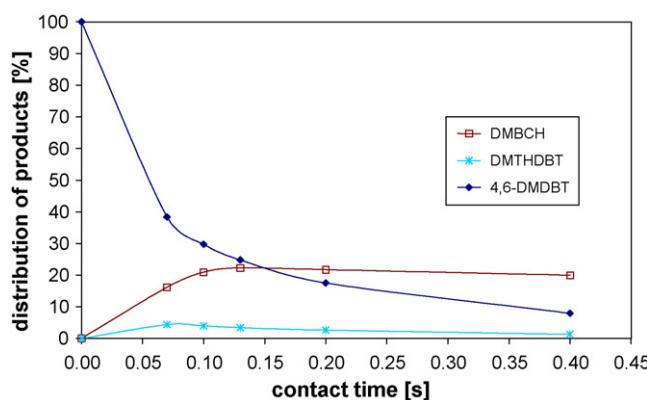


Fig. 9. Distribution of products for HDS of 4,6DMDBT versus contact time over PtSn/SiO₂ catalyst.

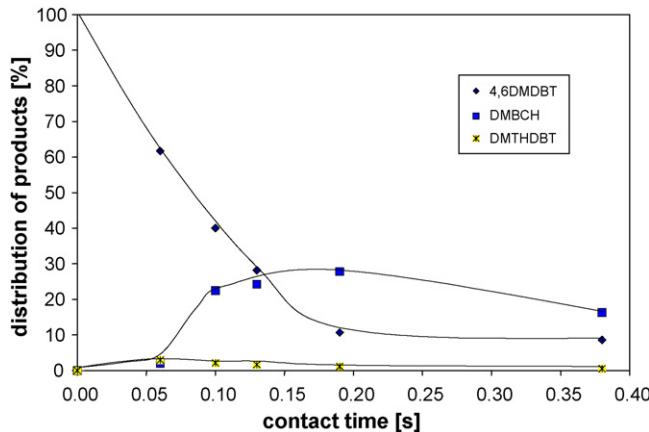


Fig. 10. Distribution of products for HDS of 4,6DMDBT versus contact time over commercial KF848 catalyst.

3.3. Hydrodenitrogenation

Fig. 11 presents results degree of hydrodenitrogenation and conversion of carbazole, while Figs. 12 and 13 illustrate the concentration changes of the reaction products in the presence of both PtSn catalysts studied. In this reaction the activity of the catalyst PtSn/SiO₂ (Fig. 11) is greater than that of the other two catalysts. The catalyst PtSn/SiO₂ gives about 80% conversion of carbazole in a relatively short contact time and complete denitrogenation is achieved for the contact times longer than 0.2 s. It has been shown that in the presence of PtSn/Al₂O₃ in the whole range of the contact times studied, the carbazole conversion was much higher than the degree of hydrodenitrogenation. On the other hand, in the presence of the catalyst PtSn/SiO₂ and the commercial KF848, the degrees of both conversion and HDN were similar especially for the contact times longer than 0.13 s, which suggested a high selectivity of this catalyst to HDN.

3.3.1. HDN over PtSn/Al₂O₃

The reaction of HDN of carbazole over PtSn/Al₂O₃ (Fig. 12) involves hydrogenation to tetrahydrocarbazole (THC) and the main product of hydrogenolysis of the C–N bond is

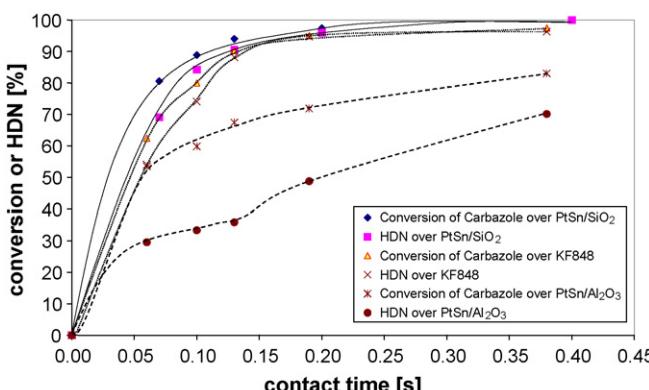


Fig. 11. Conversion and degree of HDN as a function of contact time for PtSn/Al₂O₃, commercial KF848 and PtSn/SiO₂ catalysts.

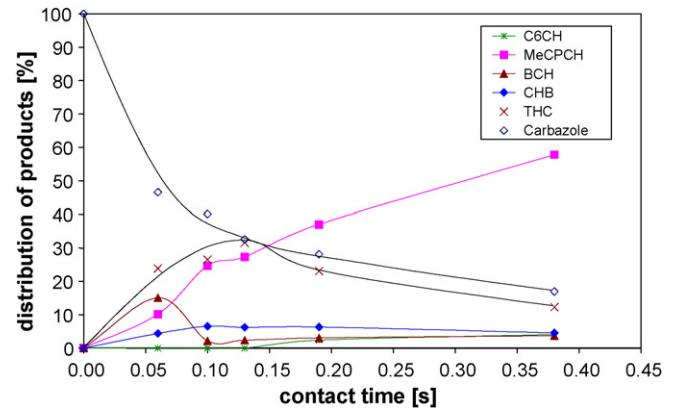


Fig. 12. Distribution of products for HDN of carbazole versus contact time over PtSn/Al₂O₃ catalyst. C₆CH–*n*-hexylcyclohexane.

bicyclohexane (BCH). The amount of cyclohexylbenzene (CHB) being the main product of direct denitrogenation (preceded only by hydrogenation of one aromatic ring) was small and maintained at a level of 5%. In the HDN reaction of carbazole, the maximum concentration of THC as an intermediate product was achieved for the time of contact of 0.13 s and it was relatively high of about 30%. This result suggests that hydrogenation of carbazole to THC over this catalyst is very easy. The rate of the total process of carbazole conversion is restricted by the rate of the THC reaction leading to the denitrogenation products. The conversion of carbazole taking place over the catalyst PtSn/Al₂O₃ can be separated into two stages. The first is the HDN of carbazole to BCH being the main product of the reaction, while the second is isomerisation of BCH as a consecutive reaction. For the contact time of 0.07 s, BCH reaches a maximum concentration giving finally methylcyclopentylcyclohexane (MeCPCH) being the final product of carbazole conversions. As follows from the data presented in Fig. 12, for the contact times longer than 0.13 s the amount of MeCPCH obtained increases in proportion to the decreasing concentration of THC.

Another important observation is that the concentration of BCH as the main reaction product reaches a maximum for the

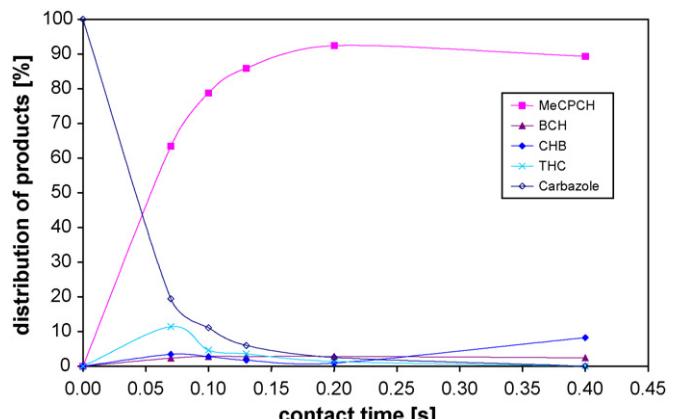
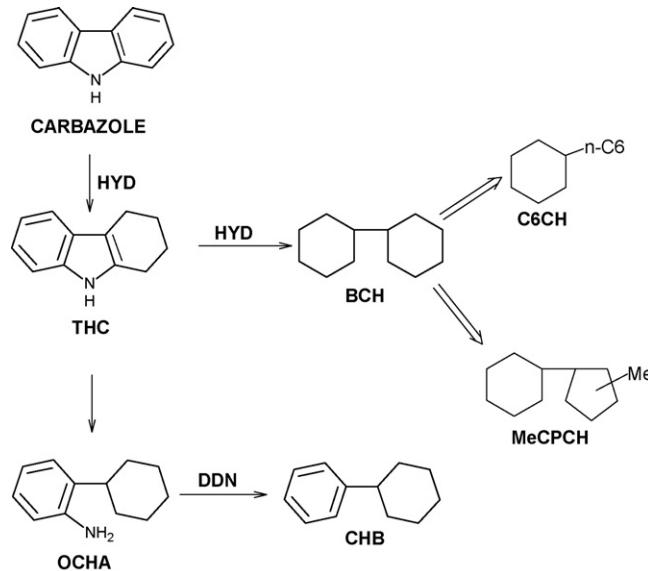


Fig. 13. Distribution of products for HDN of carbazole versus contact time over PtSn/SiO₂ catalyst.



Scheme 2. Reaction network of HDN of carbazole.

contact time of 0.07 s. As follows from Fig. 12, the final product of the process is MeCPCH obtained in the reaction of isomerisation of BCH.

The results suggest that the primarily obtained BCH for the contact times longer than 0.07 s undergoes fast isomerisation to MeCPCH whose amount increases with increasing contact time. Therefore, it seems that in the process of carbazole conversion the dominant is the consecutive reaction of isomerisation of the main denitrogenation product BCH. On the basis of the above results, Scheme 2 of carbazole transformations can be proposed.

3.3.2. HDN over PtSn/SiO_2

The catalyst PtSn/SiO_2 was particularly highly active in the HDN reaction of carbazole and in the subsequent isomerisation reaction. The distribution of the reaction products is presented in Fig. 13. Practically the only dominant product of the reaction was MeCPCH, while the contribution of the other reaction products BCH and CHB did not exceed a few percent in total. For the contact times longer than 0.25 s, the amount of CHB increased and the concentration of MeCPCH slightly decreased to about 4%. These results suggest that in these conditions dehydrogenation of BCH to CHB could occur at the expense of the isomerisation of BCH to MeCPCH. The activity of the PtSn/SiO_2 catalyst in the above reaction of isomerisation was greater than that of $\text{PtSn}/\text{Al}_2\text{O}_3$. For the former, practically the only compound obtained in the whole process of carbazole conversions was the product of BCH isomerisation (in about 90%), while BCH and CHB formed in very small amounts (Fig. 12). The concentration of the intermediate product THC reached a maximum for the contact time of 0.07 s.

The activity of PtSn/SiO_2 in the HDN reaction and in the consecutive reaction of isomerisation was very high, as for the shortest contact time applied (0.07 s) the amount of the obtained MeCPCH reached 60%, while the carbazole conversion reached over 80%.

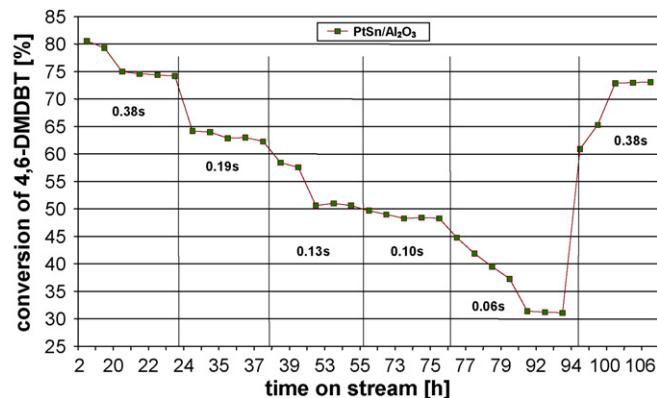


Fig. 14. Stabilisation of conversion for both PtSn catalysts versus time on stream for 4,6DMDBT.

3.4. Stabilization of catalysts

The stabilization of both PtSn catalysts for conversion of 4,6DMDBT reaction versus the time on stream is presented in Fig. 14. The catalytic process was conducted for about 100 h. After this time the initial conditions of the reaction were reset (initial contact time) and the reaction was continued to obtain stable catalytic activity again (after about additional 15 h). Since the activity returned practically to the initial level. The similarly was observed for HDN reaction for both PtSn catalysts.

4. Discussion

The main aim of the study was assessment of the activities of the catalysts PtSn/SiO_2 and $\text{PtSn}/\text{Al}_2\text{O}_3$ and a comparative analysis of their catalytic effect.

As follows from the results obtained, the reaction of HDS of 4,6DMDBT proceeds along two pathways via direct desulphurisation (DDS) and via hydrogenation HYD [6,34,35], similarly as over usually applied sulphide catalysts. However, in contrast to the sulphide catalysts, the PtSn/SiO_2 and $\text{PtSn}/\text{Al}_2\text{O}_3$ ones and in particular the former, prefer the reaction of destructive hydrogenation (hydrogenolysis of C–S bonds) of 4,6DMDBT to MCHT and to 3,3'DMBCH. This preference is related to the presence of platinum known to have shown hydrogenation–dehydrogenation properties in many other reactions [9,36–37]. With increasing contact time, the amount

of 3,3'DMBCH and MCHT formed increased, while the concentration of 3,3'DMBPh was independent of the contact time. This observation suggests that both HDS products are formed as a result of further hydrogenation of 4,6DMTHDBT, which excludes formation of 3,3'DMBCH as a product of hydrogenation of MCHT. This exclusion is related to the nonplanar structure of the MCHT molecule and thus with hindered adsorption of this compound on the catalyst surface and its further hydrogenation. No presence of more hydrogenated derivatives of 4,6DMDBT was detected among the reaction products, as they probably either undergo fast conversion to the final HDS products or their concentration is very small [34]. Besides showing high activity, both PtSn catalysts are also characterised by much greater resistance to deactivation with the sulphur compounds occurring in the reaction mixture (300 ppm S as 4,6DMDBT) than that of the monometallic catalyst Pt/Al₂O₃, quickly undergoing deactivation in the presence of sulphur. In the simultaneously conducted HDS and HDN reactions the presence of tin significantly increases the stability and activity of the platinum catalyst. This effect follows from a commonly known positive influence of tin in different catalytic reactions, mentioned in the introduction [17–20,35]. It is reasonable to suppose that the high activity of PtSn catalysts in the reactions studied is also a result of increased stability and resistance to coking of the platinum catalysts containing tin [17,21,38]. In our reactions both PtSn catalysts were stable after 100 h of reaction—because the activity returned practically to the initial level, it has been concluded that deactivation of the PtSn catalysts do not take place (see Fig. 14 and Section 3.4).

It seems that the high activity of the catalysts PtSn/SiO₂ and PtSn/Al₂O₃ is also a consequence of their resistance to sulphur poisoning. It is well known that the catalysts containing noble metals are characterised by very high activity, but in the presence of a relatively small amount of sulphur they are quickly deactivated [16,38]. Sulphur even in low amounts causes permanent poisoning of the metallic centres of the catalyst. The sulphur compound present in the raw product is reversibly adsorbed at the metallic site containing sulphur already, and this adsorption depends on the temperature and partial pressure of a given sulphur compound [39]. The two types of sulphur together totally inhibit the catalytic activity related to the catalytic centres [39]. Moreover, sulphur not only poisons the metallic centres but also affects the activity related to the metal/acid functions [39]. The addition of tin is thus supposed to increase the number of electron-deficient metal sites that enhance the catalyst resistance to sulphur poisoning. This increase reduces the irreversible adsorption of sulphur and decreases the amount of coke whose formation is stimulated by the presence of sulphur [40]. On the other hand, metal sites poisoned by sulphur are incapable of H₂ activation and an addition of tin causes an increase in the hydrogen spillover of the catalyst [41]. It is particularly important for the HDN process in which the hydrogenating properties play a substantial role [7,42]. The above suppositions have been confirmed by the results obtained, proving that the catalyst PtSn/SiO₂ is much more active in HDN than the commercial one.

Analysis of the distribution of the products formed in the reaction of hydrodesulphurisation of 4,6DMDBT over PtSn/Al₂O₃ (Figs. 6 and 8) and over PtSn/SiO₂ (Figs. 6 and 9) indicates the differences in the selectivity of these two catalysts. The main product of the HDS reaction over PtSn/Al₂O₃ is 3,3'DMBCH, and over PtSn/SiO₂ is MCHT. The differences in the catalytic behaviour of these two catalysts follow from the properties of the support: Al₂O₃ is acid–basic and SiO₂ is weakly acidic. Thus, the results indicate that the acidic centres influence the completion of hydrogenation of 4,6DMTHDBT to 3,3'DMBCH [43]. The differences in the catalytic performance are also related to the type and amount of the metallic phases present on the support surface determined by the acidic character of the support. In Al₂O₃ a certain fraction of tin reacts with the support and thus tin occurs in the oxidation degree higher than zero, forming tin aluminate and therefore, changing the acidic character of the support and increasing the dispersion of Pt, as has been noted already by Baris et al. [18]. In SiO₂ a greater fraction of tin undergoes reduction forming different type alloys with Pt and other surface groups [18,38]. In the process of hydrogenation, the Brønsted acidic centres play an important role and their presence on the PtSn catalyst supported on the Al₂O₃ support can lead to obtaining the fully hydrogenated reaction product that is 3,3'DMBCH. Thus, the hydrogenating properties of PtSn/Al₂O₃ are a resultant of the hydrogenating function related to the metal and that related to the acidic centres, which is consistent with the postulates of [44].

In the HDN reaction of carbazole the differences in the catalytic performance of the two catalysts are even more pronounced (Figs. 12 and 13). The main reaction pathway involves hydrogenation via the intermediate THC to BCH as the main product and a small amount of CHB [45,46]. The BCH formed in this reaction is rapidly converted into MCPCH as a result of the consecutive reaction of isomerisation. The reaction of isomerisation leading to products containing the methylcyclopentane ring, is related to the metallic activity of the catalyst [41,47,48]. Beltramini and Trimm [49,50] also reported that an addition of tin to the platinum catalyst increased the effectiveness of the isomerisation. Hence, it can be expected that the strong metallic properties responsible for the high activity of PtSn/SiO₂ are first of all related to the presence of PtSn alloys of different composition [51]. It has been shown [38] that the type of support has a significant influence on formation of different type surface bimetallic groups supported on Al₂O₃ and SiO₂ [38]. The formation of different bimetallic groups can be related to the complex effect of tin responsible for an increase in the activity of the platinum catalyst and enhancement of its resistance to sulphur poisoning [19,52]. The above-mentioned reports are confirmed by our results indicating a higher activity of PtSn/SiO₂ than PtSn/Al₂O₃ catalyst, in particular in the reaction of isomerisation of the HDN products of carbazole. As mentioned earlier, when Al₂O₃ is used as a support, some fraction of tin forms on its surface some chemical structures and thus the amount of tin available for formation of surface groups with Pt is reduced. When SiO₂ is used as a support the whole amount of tin present on the surface is available for formation of different bimetallic groups with Pt [19,36]. The type and number of these groups depend on a

number of factors, mainly on the preparation method and the concentrations of Pt and Sn. As far as the preparations studied are concerned, the fact that they were subjected to direct reduction without preliminary calcination could also have affected their activity.

The large differences shown in the hydrotreating activity specially in the HDN reaction between PtSn catalysts supported on Al_2O_3 and SiO_2 result from the physicochemical properties of both samples. The significantly higher CO chemisorption for PtSn/ SiO_2 indicates the presence of larger amount of metallic species and better hydrogenation properties so important for deep hydrotreating process.

5. Conclusions

The use of PtSn catalysts supported on Al_2O_3 and SiO_2 in the simultaneous reactions of HDS of 4,6-dimethyldibenzothiophene (4,6DMDBT) and HDN of carbazole has shown their high catalytic activity.

The catalyst PtSn/ SiO_2 was found more active than PtSn/ Al_2O_3 and the commercial catalysts KF848 in the reactions of HDS of 4,6DMDBT and HDN of carbazole. The activity of PtSn/ Al_2O_3 for the all range of contact time was lower for both reaction—HDS and HDN comparison to PtSn/ SiO_2 and KF848 catalysts.

The reaction of hydrogenation of 4,6DMDBT occurs over both PtSn catalysts studied, however, the dominant product obtained over PtSn/ Al_2O_3 is MCHT, while over PtSn/ SiO_2 is 3,3'DMBCH. The amount of the obtained 3,3'DMBPh was small and practically independent of the contact times used. In the HDN reaction the PtSn/ SiO_2 catalyst was particularly active leading to BCH as the main product. The catalysts PtSn/ Al_2O_3 and PtSn/ SiO_2 were also characterised by high activity in the reaction of carbazole isomerisation to MCPCH. For the catalyst PtSn/ SiO_2 the compound MCPCH was the dominant product as its yield was higher than 90%.

It has been shown that the activity of the PtSn catalysts studied is highly dependent on the type of support and thus on the composition of the surface phase of the catalyst.

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